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Impedance Studies of the Cell Pt/ Ag⁺ Conducting Glass/
Ag Beta" Alumina/Pt

by

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IMPEDANCE STUDIES OF THE CELL Pt/ Ag^+ CONDUCTING GLASS/ Ag BETA"
ALUMINA/ Pt

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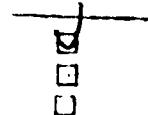
ABSTRACT

The qualitative comparison of the impedance behavior of the three cells Pt/ Ag^+ conducting glass / Ag beta" alumina/ Pt, Pt/ glass/ Pt and Pt/ beta"/ Pt leads to the conclusion that the properties of the cell Pt/ glass/ beta"/ Pt are determined by those of the interfaces Pt/ glass and beta"/ Pt at low and intermediate frequencies. At high frequencies the contributions of the bulk impedances become predominant. A contribution from the impedance of the interface glass/ beta" is small with respect to the other contributions. The transfer of the Ag^+ ion from the amorphous glass phase into the crystalline beta" alumina is rapid.

INTRODUCTION

Studies of the kinetics of the transfer of the conducting ion from a solid electrolyte 1 into an electrolyte 2 have been mainly carried out in systems where the electrolyte 2 was liquid. Aqueous electrolytes were used for silver ion conductors, especially AgI (1 - 4) and Ag_3SI (5,6). Sodium ion conductors were investigated (7,8) in organic electrolytes.

Little work has been reported (9,10) for systems in which both electrolytes were solids. A previous paper (11) involved impedance studies of the symmetrical cell $\text{Ag}/ \text{AgI}/ \text{Ag}$ beta" alumina/ $\text{AgI}' \text{Ag}$. An attempt was made there to obtain information on the silver ion transfer between two crystalline solid electro-



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lytes. General interest exists in studies of the properties of the interface between two solid electrolytes for batteries (12) and sensors (9,13).

The asymmetric cell Pt/ Ag^+ conducting glass/ Ag beta" alumina/ Pt was chosen here. This cell incorporates an interface between an amorphous and a crystalline solid electrolyte. Pt electrodes were taken because previous work (14) on the interface Ag/ Ag beta" alumina revealed a relatively complicated behavior. Impedance spectroscopy served again as the technique in the present work.

EXPERIMENTAL SECTION

The silver ion conducting glass consisted of 34 mole% AgI, 26 mole% Ag_2O and 40 mole% B_2O_3 . It was chosen because of its relatively high glass transition temperature of 340°C . Thin slices of this glass were attached to a rectangular piece of Ag beta" alumina, obtained by ion exchange of Ceramatec Na beta" alumina. This was accomplished by heating the glass on top of the polished ceramic to just below its melting temperature and turning the furnace off. The glass surface was polished by hand. Platinum was sputtered onto the glass surface on one side and onto the polished surface of the ceramic on the other side. Contacts between the platinum films and the wire leads of the measuring system were made by silver paint. The cell was inside a glass vessel under N_2 . The glass vessel was inside a furnace heated by DC current. The temperature was controlled by a temperature controller.

The measurements of the cell impedance were made at constant temperature in the frequency range 10^{-2} to 10^5 Hz by the IM 5E automated impedance meter of Zahner-elektrik (F.G.R.). It was

found necessary to heat the cell to the highest temperature (320°C) and start the measurements there. Subsequently the temperature was decreased stepwise to room temperature and increased again. Reproducible results could be obtained if the measurements were repeated in this way.

For comparison similar measurements were carried out under the same conditions on the simpler cells Pt/ Ag^+ conducting glass/ Pt (15) and Pt/ Ag beta" alumina/Pt.

RESULTS

Results of the impedance measurements are shown at three different temperatures for the said cells in Fig.1 to Fig.3. The data are presented in a Bode plot which is directly available by a program delivered with the impedance meter. In general, plots of this type were found satisfactory for the interpretation.

DISCUSSION

The cell impedance consists of:

$$(1) \quad Z = z_{\text{Pt/glass}} + z_{\text{glass/beta}''} + z_{\text{beta}''/\text{Pt}} + z_{\text{glass}} + z_{\text{beta}''}$$

Three interfacial impedances ($z_{\text{Pt/glass}}$, $z_{\text{glass/beta}''}$, $z_{\text{beta}''/\text{Pt}}$) and two bulk impedances (z_{glass} , $z_{\text{beta}''}$) are involved. Excepting the lower temperature range, the impedances z_{glass} and $z_{\text{beta}''}$ may be considered ohmic in the frequency range under consideration here. It will be shown subsequently that this statement is in agreement with the experimental results.

It was planned originally to determine the interfacial impedances $z_{\text{Pt/glass}}$ and $z_{\text{beta}''/\text{Pt}}$ separately from the measurements on the cells Pt/ glass/ Pt and Pt/ beta"/ Pt and to subtract the values at a given frequency and temperature from those of Z .

However, the reproducibility of the impedance data from cell to cell was found to depend strongly upon the preparation of the sputtered electrodes and their heat treatment. Thus the outlined procedure had to be replaced by a qualitative comparison of the impedance plots.

The plots of the logarithm of the absolute value of the cell impedance versus the logarithm of the frequency display a relatively simple behavior at 150° and 300°C in Fig.1 and at all three temperatures in Fig.2. The absolute values decrease and approach a practically constant value at high frequencies. The constant value can be assigned to $R_{\text{glass}} + R_{\text{beta}}''$ in Fig.1 and to R_{glass} in Fig.2. The bulk resistances R_{glass} and R_{beta}'' were also estimated from separate four-probe measurements of the bulk conductivities of the two solid Ag^+ ion conductors and the geometric dimensions. The computed values agreed reasonably well with the experimental values at high frequencies at the said temperatures. The fact that R_{glass} is considerably smaller than R_{beta}'' is reflected by the lower values of Z in Fig.2 than in Fig.1 at high frequencies. The absolute value of the impedance does not approach a constant value at high frequencies at 25°C in Fig.1 because the influence of the grain boundary impedance on Z_{beta}'' becomes visible at the low temperature. A different effect is responsible that R_{beta}'' is approached in Fig.3 at high frequencies, but not reached. It is suggested that an additional process the nature of which is not known at present becomes effective at high frequencies. It is not possible to separate the contribution of this process from bulk contributions.

The phase angle and the absolute value of the impedance in Fig.1 and Fig.3 display the properties of a constant phase element at low frequencies in a first approximation. In Fig.2

such a behavior is only seen at 25° C. The latter result can be explained by a system with blocking electrodes. The phase angle approaches values which do not differ much from 90° (theoretical value of a capacitor). Somewhat lower average values of the phase angle are observable at low frequencies in Fig.1. While these values in Fig.1 might still be assigned to an interface with blocking electrodes, this is not feasible in Fig.3 any longer. The average values of the phase angle at low frequencies have become too different from 90° to assign them to blocking electrodes. Probably Faradaic processes at the interface beta"/ Pt are involved. The reader is referred for a discussion of the results at 150° and 300° in Fig.2 to reference 15.

The qualitative comparison of the low- frequency behavior of the cell impedances shows that the properties of the cell Pt/ glass/ beta"/ Pt lie between those of the cells Pt/ glass/ Pt and Pt/ beta"/ Pt. It appears that the contributions of both interfaces (Pt/ glass and beta"/ Pt) to the impedance determine its behavior.

The behavior of the impedance of the cell Pt/ glass/ beta"/ Pt could be interpreted in a qualitative fashion for low and high frequencies. A contribution of the interface glass/ beta" to the total impedance could not be detected. It has to be small with respect to the other contributions. It follows that the transition of the Ag⁺ ion from the amorphous electrolyte into the crystalline electrolyte has to be rapid.

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FIGURE CAPTIONS

Fig.1: Bode plot of impedance data for the cell Pt/ Ag^+ conducting glass/ Ag beta" alumina/ Pt at different temperatures.

Fig.2: Bode plot of impedance data for the cell Pt/ Ag^+ conducting glass/ Pt at different temperatures.

Fig.3: Bode plot of impedance data for the cell Pt/ Ag beta" alumina/ Pt at different temperatures.

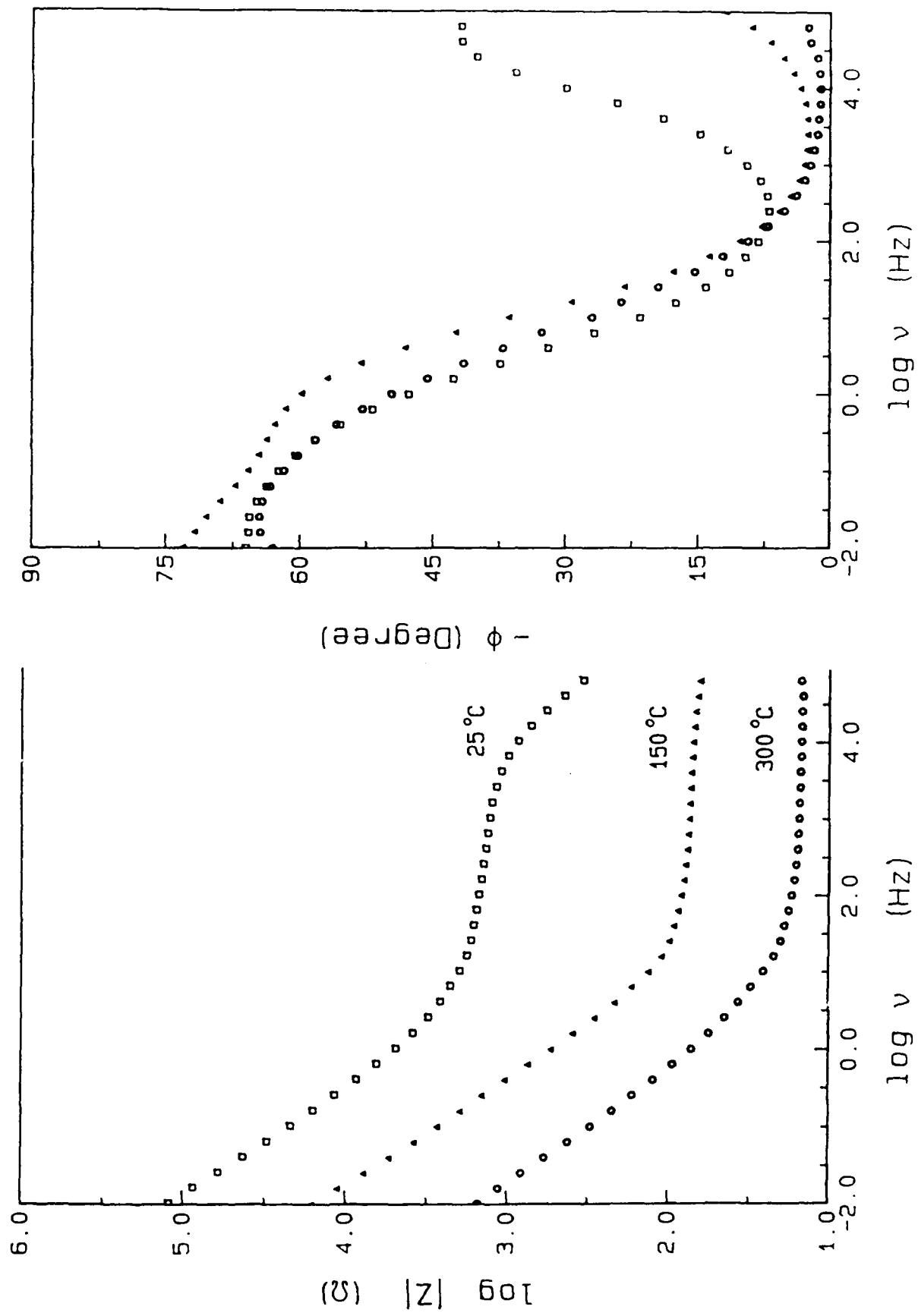


Fig. 1

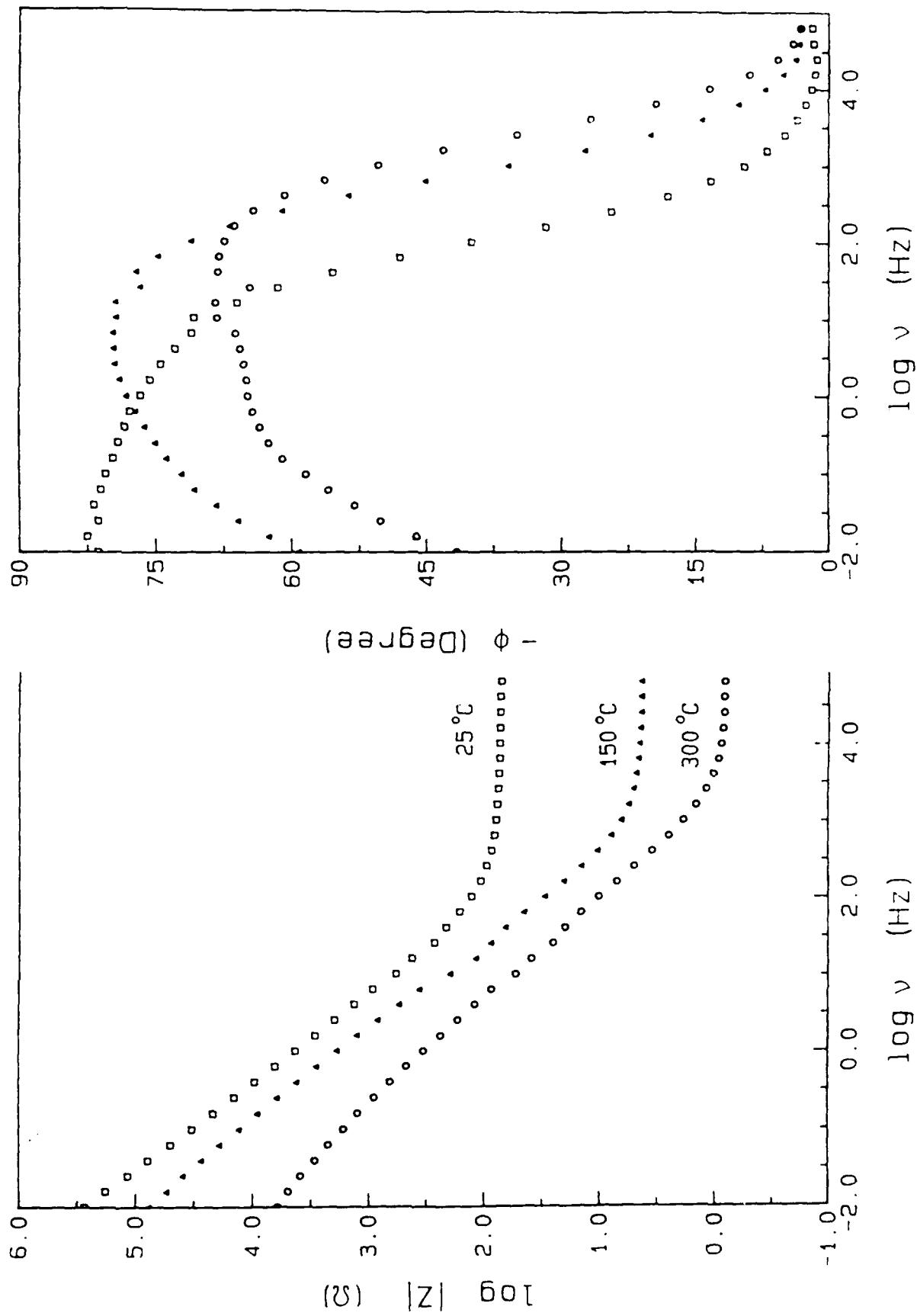


Fig.2

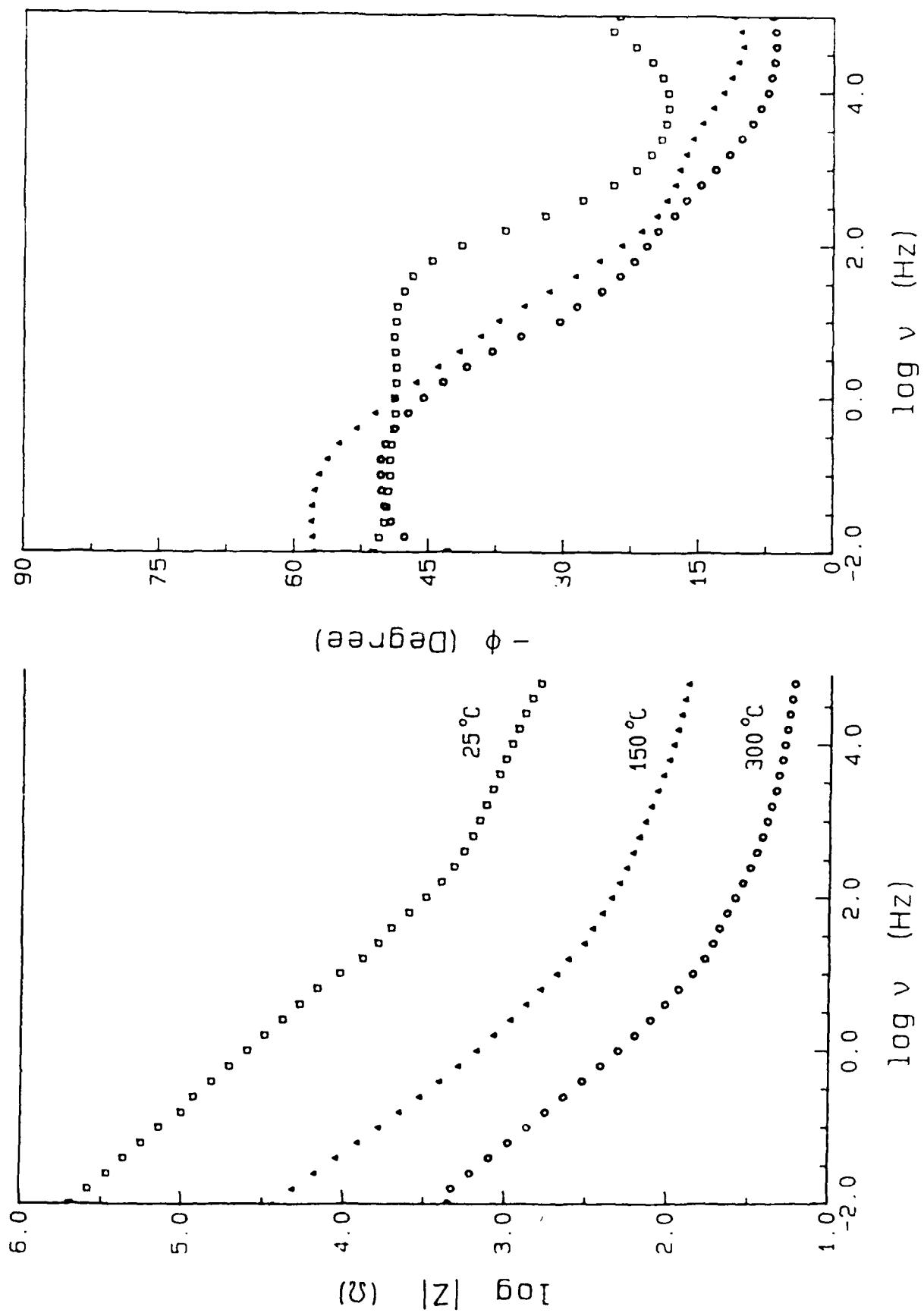


Fig. 3